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16. ABSTRACT The paper discusses the fundamental processes in sulfur dioxide (SO2) capture by calcium-based adsorbents for upper furnace, duct, and electrostatic precipitator (ESP) reaction sites. It examines the reactions in light of controlling mechanisms, effect of sorbent physical properties, and important process variables. Upper furnace reactivity is limited to 900-1200 C by rate and equilibrium constraints, respectively. Sulfation is a function of in-situ sorbent characteristics of porosity, particle size, and surface area. Conversion of the sorbent is ultimately limited by the formation of the calcium sulfate (CaSO4) product layer. The in-duct reaction is accomplished through sorbent scavenging in the flue gas stream by a water spray. The scavenging efficiency of the sorbent by the water droplets limits the process, while reaction is controlled by the dissolution rate of the sorbent. The E-SOX process in a modified ESP simulates a short time spray dryer through injection of a calcium hydroxide--Ca(OH)2--slurry. The Ca(OH)2 undergoes aqueous phase reaction to remove SO2. Evaporation of the droplets prior to the ESP field conditions the flue gas for more efficient particulate matter collection by lowering the gas resistivity.

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FUNDAMENTAL PROCESSES INVOLVED IN SO_2 CAPTURE BY CALCIUM-BASED ADSORBENTS

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ABSTRACT

The fundamental processes in sulfur dioxide (SO_2) capture by calcium-based adsorbents are presented for upper furnace, duct, and electrostatic precipitator (ESP) reaction sites. The reactions are examined in light of controlling mechanisms, effect of sorbent physical properties, and important process variables. Upper furnace reactivity is limited to the temperature range of 900 to 1200 °C by rate and equilibrium constraints, respectively. Sulfation is a function of in-situ sorbent characteristics of porosity, particle size, and surface area. Conversion of the sorbent is ultimately limited by the formation of the calcium sulfate ($CaSO_4$) product layer. The in-duct reaction is accomplished through sorbent scavenging in the flue gas stream by a water spray. The scavenging efficiency of the sorbent by the water droplets limits the process, while reaction is controlled by the dissolution rate of the sorbent. The E-SOX process in a modified ESP simulates a short time spray dryer through injection of a calcium hydroxide [$Ca(OH)_2$] slurry. The $Ca(OH)_2$ undergoes aqueous phase reaction to remove SO_2. Evaporation of the droplets prior to the ESP field conditions the flue gas for more efficient particulate matter collection by lowering the gas resistivity.

INTRODUCTION

Extensive research on the removal of SO_2 from utility flue gas by calcium-based adsorbents has focused on three technologies: upper furnace injection, duct humidification, and the E-SOX process. The dry sorbent process was initially conceived as burner injection of calcium carbonate ($CaCO_3$), calcination to the reactive form CaO, and then reaction with SO_2 to form $CaSO_4$. This process has been improved to involve upper furnace injection of primarily $Ca(OH)_2$ sorbents beyond the high temperatures of the burner zone. Current research has focused on attaining the maximum sorbent conversion possible since that has been identified as the most direct means of improving process economics. This has involved fundamental research aimed at understanding the effect of sorbent physical parameters upon reactivity, the phenomena occurring at times under 100 ms, the causes and role of sintering in the sorbent deactivation process, and the effect of various hydration additives upon the performance of $Ca(OH)_2$ sorbents.

Additional capture by the partially sulfated sorbent can be obtained following upper furnace sorbent injection by duct humidification. The sorbent is collected into the water spray droplets (scavenged) through inertial impaction mechanisms. The resultant slurry droplets undergo aqueous phase reaction with absorbed sulfur. Research is now involved in maximizing sorbent scavenging, limiting process impacts upon furnace operation, and maximizing sorbent reactivity.

The E-SOX process operates like a conventional, short time, spray drier through injection of a sorbent-water slurry into an ESP section with its collection plates removed. The E-SOX process results in added SO_2 capture and enhanced ESP collection efficiency due to the lowered resistivity caused by water spraying. Significant questions to be resolved include the effects of Ca/S ratio, the approach to adiabatic saturation, and SO_2 concentration upon the reactivity of the slurry.

In this paper, the three SO_2 removal processes of upper furnace sorbent injection, duct spraying, and E-SOX are discussed in terms of reaction mechanisms, limiting process variables, and current research needs. This paper presents a survey of the current state of development of these three processes, summarizing recent findings and remaining issues.

UPPER FURNACE SO_2 REMOVAL

Injection of $Ca(OH)_2$ or $CaCO_3$ into the upper furnace results in thermal activation to the reactive form, calcium oxide (CaO). The subsequent, overall reaction has the form

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4.$$

Equilibrium considerations favor the formation of the $CaSO_4$ product up to around 1200 °C for typical SO_2 concentrations. Below 900 °C, the reaction is generally considered to be too slow for practical applications. These two temperatures define the boundaries of what is called the sulfation "window." The residence time of the reactive sorbent in this window is determined from the furnace quench rate. For example, a quench rate of 300 °C/s (540 °F/s) results in a 1 s residence time. The optimal furnace injection temperature has been found to be about 1300 °C (Overmoe et al., 1986), although the cooling effect of the sorbent carrier gas reduces this to about 1200 °C. This temperature is likely the optimal result of the interaction of the activation and sulfation processes. Laboratory scale isothermal reactors have found optimal injection temperatures to be lower, around 1100 °C (Cole et al., 1985a). This is likely due to a tradeoff between reactivity and sintering.

Although most of the early sorbent injection work was done with $CaCO_3$ (Coutant et al., 1971; Ishihara et al., 1975; Borgwardt and Harvey, 1972), more recent work has almost exclusively focused on the use of $Ca(OH)_2$ (Overmoe et al., 1986; Snow et al., 1986; Gooch et al., 1986). Although dolomitic sorbents ($CaCO_3$-$MgCO_3$) have shown superior reactivity (Cole et al., 1985b), the hydroxides are more economical on an equal basis. $Ca(OH)_2$ has the benefits of high reactivity and low mass per Ca^{++}. The higher reactivity found with hydroxides is currently thought to be primarily due to a smaller particle size distribution (Borgwardt et al., 1987). Indeed, some work with production of $Ca(OH)_2$ under high pressure conditions (Weber et al., 1986) has resulted in higher SO_2 capture than the atmospherically produced $Ca(OH)_2$. This advantage is thought to be due to a smaller particle size distribution produced during the pressure hydration process.

Economical operating conditions generally assume sorbent injection at a Ca/S ratio of 2.0. At these levels, the SO_2 removal for $Ca(OH)_2$ injection typically ranges from 50 to 60%.

The mass median particle size (D_{50}) of hydroxide sorbents is typically 2-3 μm (Fig. 1). Production of a $CaCO_3$ sorbent to this size by crushing and grinding processes is uneconomical (Thompson, 1985). Typical surface areas of the raw $Ca(OH)_2$ sorbents range from 10 to 20 m^2/g, reflecting both the high external specific surface area of small particles and an even greater amount of internal surface area. The internal surface area of the raw hydroxide sorbents is reflected by porosities of around 0.15.

The activation process results in the development of considerable internal surface area and porosity. During this process, the hydroxide loses its chemically bound water to form CaO. This is generally thought to occur within milliseconds of sorbent injection.

The sulfation process occurs sequentially or consecutively with that of the activation process. The mechanistic steps include: a) diffusion of gaseous SO_2 to the sorbent particle surface, b) SO_2 diffusion through the pore structure of the sorbent, c) diffusion through the built up $CaSO_4$ product layer, and d) heterogeneous chemical reaction at the CaO/$CaSO_4$ interface. Sulfation occurs rapidly (Fig. 2) upon the exposed external and internal surface area of the CaO, building up a $CaSO_4$ product layer. Considerable variation exists between the mechanistic theories of involved researchers. One theory suggests that suitable conditions will lead to continued chemical reaction rate control (Simons, 1987), another suggests that product filling of the pore structure will lead to gaseous pore diffusion control (Newton and Pershing, 1987), and a third proposes that the rate of reaction is controlled wholly by ionic diffusion through the $CaSO_4$ product layer (Borgwardt et al., 1987).

The role of the physical properties of the sorbent is much clearer than the mechanistic theories of the process. The effects of surface area and porosity upon reactivity have been well documented. The rate constant for product layer diffusion control has been related to the square of the initially developed surface area (Borgwardt and

Bruce, 1986). Hartman et al. (1978) noted that the conversion of CaO to $CaSO_4$ increases with the available pore volume of the unsulfated calcine.

The pore shape of the calcined $CaCO_3$ has been shown to have a cylindrical structure, while the CaO derived from $Ca(OH)_2$ is more of a sheet or plate-like structure (Gullett and Bruce, 1987a). The pore system of the latter forms a wider size distribution (plate separation of about 50 to 600 Å) with larger pores. Although sulfation models have defined optimal pore size distributions (Newton and Pershing, 1987), currently no experimental evidence exists relating the distribution to the conversion.

The effect of sorbent particle size upon reactivity is of the order of -0.20 to -0.35 (Fig. 3). This has been confirmed by numerous researchers using pre- and post-reactor sizing methods (Ishihara et al., 1975; Gullett and Blom, 1987b; Snow, 1985). Gullett and Blom found no limit to this particle size effect upon higher reactivity over the range of 0.72 to 12.1 μm. This is contrary to expectations (Cole et al., 1986) that below 2-5 μm in size, particle size ceases to influence reactivity due to elimination of pore diffusion limitations. This effect of smaller particle sizes is likely a main reason for the higher sulfur capture observed with use of $Ca(OH)_2$ sorbents than $CaCO_3$ sorbents.

Deactivation processes are attributed to thermal sintering of the reactive CaO and the buildup of the $CaSO_4$ product layer. Sintering results in reduced surface area and pore volume, hence, lower sorbent reactivity. Sorbent sintering is promoted by the presence of CO_2 (Borgwardt et al., 1987), H_2O (Anderson et al., 1965), and possibly $CaSO_4$ itself (Glasson, 1967).

The overall furnace injection reaction involves the complex coupling of these processes of activation, sulfation, and deactivation. Numerous models have been proposed to do this. These have included grain models (Pigford and Sliger, 1973; Hartman and Coughlin, 1976), a pore tree model (Simons and Garman, 1986), and distributed pore models (Newton and Pershing, 1987; Yu and Sotirchos, 1987; Christman and Edgar, 1983). These model types assume spherical, calcined particles, while another model assumes parallel wedge-shaped pores (Dennis and Hayhurst, 1986) approximating the geometry determined by Gullett and Bruce (1987a). The latter two models use cylindrical pores.

The grain model treats the CaO particle as an agglomerate of individual grains sized to match the BET surface area. Sulfation occurs on the grain surface, altering the porosity and surface area. The reaction can be limited by product layer buildup, either through coating the grains or blocking access to the particle interior.

The distributed pore model (Newton and Pershing, 1987) assumes that the particle is composed of non-intersecting pores and matches the pore size to the analytically determined distributions from mercury and nitrogen porosimetry. $CaSO_4$ product builds up on the external and internal particle surfaces, changing the pore geometry. The reaction is limited in this model either by product plugging of small pores at the pore mouth and/or simultaneous product filling of the large pores. The chemical rate constant is assumed to be large and not rate controlling.

The pore tree model envisions the pore structure as a series of various sized trees whose trunks are located at the particle surface. The branches of the tree describe a progression of pore sizes. As in the distributed pore model, the reaction is limited by pore filling and plugging.

Each model includes the resistances due to: a) external mass transfer of SO_2 from the bulk phase to the particle surface, b) diffusion of SO_2 from the particle surface through the interior pore structure, c) diffusion of the reactant sulfur species through the product layer, and d) heterogeneous chemical reaction to form $CaSO_4$.

Variation continues to exist in the chemical constants used to model the rate of the sulfation reaction. The order of the reaction with respect to SO_2 concentration has been found to range between 0.5 and 0.62 (Coutant et al., 1971; Snow, 1985; Borgwardt and Bruce, 1986), while others claim an order of unity (Simons et al., 1987). Activation energy values of 36.6 kcal/mole (Borgwardt and Bruce) and 33.7 kcal/mole (Simons) are close to each other, but are attributed to different mechanisms of ionic product layer diffusion and chemical reaction control, respectively.

The importance of particle size upon sorbent reactivity and the difficulties with $Ca(OH)_2$ agglomeration (Gullett and Blom, 1987b) have led to considerable efforts in the hydration process to develop finer and less agglomerative products. Current efforts with hydration water additives such as chemical surfactants have improved SO_2 capture around 15% (Gooch, 1987). Although it is not known whether this is due to production of smaller particles or prevention of particle agglomeration, the latter is the more likely explanation.

Significant questions remain to be answered before a full understanding of the high temperature CaO/SO_2 reaction will be obtained. The coupling of the activation and sulfation processes reaches completion within a few hundred milliseconds of injection. Enhancement of these short time phenomena may significantly remove the residence time constraints due to the quench rate within the sulfation window. The effect of hydration additives remains unknown and represents an effective way of improving capture. Work on the effect of CO_2- and H_2O-promoted sintering is scarce, although fundamental toward retention of sorbent reactivity. The argument over controlling reaction mechanisms remains to be resolved.

DUCT SPRAYING

Duct spraying was conceived as an extension of upper furnace sorbent injection. An injected water spray scavenges partially reacted sorbent, resulting in aqueous phase SO_2 capture. The slurry droplet evaporates, and the remaining solids are captured by the existing particulate collection devices. The humidification process also has the benefit of improving the ESP performance by lowering the gas resistivity.

The process involves the following interactive steps. The sorbent is scavenged by the injected water spray, principally by a mechanism of inertial impaction, forming a slurry. SO_2 diffuses to the droplet, and is absorbed and ionized to form HSO_3^- and H^+. The CaO reacts with the droplet water to form $Ca(OH)_2$. $Ca(OH)_2$ dissolves into solution resulting in a flux through a film surrounding the solid particle. The $Ca(OH)_2$ chemically reacts with the HSO_3^- to form a $CaSO_3 \cdot H_2O$ precipitate. The slurry droplet evaporates leaving the partially reacted solid particle.

The duct spraying process must be designed to minimize the unwelcome prospect of wall wetting and solids deposition. Therefore, the injector variables (spray angle, air/water ratio, and nozzle positioning) and resultant droplet size and approach to adiabatic saturation must be adjusted to evaporate the spray droplets prior to wall impaction. This must be accomplished while maximizing the amount of time the sorbent remains in the reactive aqueous state.

SO_2 capture by the spraying process is limited by the amount of sorbent scavenged by the water spray and the reactivity of the resultant slurry. Recent experiments with spray nozzles in a sorbent laden duct measured scavenging by a laser diagnostic technique (Newton, 1987). These efforts to maximize scavenging efficiency suggest that typical values around 15 to 25% sorbent capture can be expected. Adjustment of the air to water (A/W) injection ratio in a twin-fluid spray nozzle provides some control of scavenging through changing the droplet diameter and velocity. A higher A/W ratio imparts more of the air's momentum to the water droplets, resulting in a higher droplet velocity while decreasing drop size. Lower A/W ratios increase the number of drops and their size, while decreasing the droplet velocity. A larger droplet diameter and a higher differential velocity between the water droplets and gas-entrained sorbent both result in greater scavenging efficiency. Because each is effected by different directions of the A/W ratio, an optimum case exists. The net result is a cancelling effect, implying that scavenging has only a weak dependency upon the A/W ratio.

An even distribution of the spray across the face of the duct (spray angle adjustment) does not appear to enhance scavenging. However, scavenging is enhanced at reduced flue gas velocities or by concentration of the solids into the water stream. Experimental and modeling efforts show that a reduction of duct velocity increases scavenging, given a constant water spray amount (Fig. 4). An increase in the gas/sorbent residence time in the high efficiency scavenging zone near the nozzle causes an increase in sorbent scavenging. Although boiler turndown reduces gas flowrates, the water spray amount also has to be reduced to maintain the approach to saturation, leaving scavenging unaffected. An increase in the duct cross-sectional area will

likewise reduce the gas velocity, but will also reduce the sorbent flux into the scavenging zone, resulting in no added scavenging benefits.

Model and experimental work shows that concentration of the sorbent near the nozzle without alteration of the flow fields will aid scavenging (Fig. 5) (Newton, 1987). This approach increases the sorbent density near the water injector without changing its residence time in the high scavenging region.

The main problem with maximizing scavenging is that the necessary methods are at variance with the engineering requirement to prevent significant wall wetting. Larger drops and higher velocities scavenge more sorbent but also take longer to evaporate. If droplets do not evaporate by the time they encounter bends in the duct, they are likely to wet the walls, causing a slurry buildup.

A single droplet, drop tube reactor was developed to investigate the limits to slurry reaction decoupled from evaporation (Newton, 1987). Experiments have examined the effects of SO_2 concentration, slurry concentration, and approach to saturation. The rate of conversion is proportional to SO_2 concentration up to 800 ppm SO_2 (Fig. 6), indicating that the reaction is limited by the external transport of SO_2 to the droplet. Beyond 800 ppm SO_2, the level of calcium utilization is constant, suggesting that the availability of the dissolved Ca^{++} is rate limiting.

Increases in the slurry concentration show decreasing utilization (Fig. 6) resulting in a decline in the incremental sulfur capture. Even though calcium availability controls the reaction at high SO_2 concentrations, the appearance of additional sorbent in the slurry reduces specific calcium availability. This suggests that efforts to enhance scavenging efficiency, leading to increased slurry concentration, may be offset by a decrease in apparent sorbent reactivity.

The principal effect of a low approach to saturation is to delay the evaporation of the slurry into the dry, unreactive state. Since the dissolution of Ca^{++} appears to be the rate limiting step at typical duct SO_2 concentrations, the extent of reaction will depend strongly on droplet lifetime (Fig. 7).

Efforts to increase the rate of Ca^{++} dissolution with additives are in progress. Additives that have been tested were selected to prevent intradroplet solids agglomeration, alter the pH of the solution, or modify the product layer diffusivity. Preliminary results have suggested that hydrates with higher surface areas are superior, probably due to the area effect upon the dissolution rate of the sorbent.

Current duct spraying models include one and two dimensional formulations involving sorbent capture, droplet evaporation, and reaction predictions. The models couple the parameters of droplet number, size, and velocity to determine the effect upon scavenging without adjustable parameters. Agreement with measurable trends and values validates the model's representation of these fundamental processes (Newton, 1987).

Considerable research effort remains warranted in such areas as enhancing the Ca^{++} dissolution rate; understanding the effects of slurry concentration, sorbent structure, and size; and improving sorbent scavenging within the context of proper furnace operation and minimal wall wetting.

E-SOX

The E-SOX process was conceived as a low cost retrofit technology for existing ESP systems to remove SO_2 and particulate matter. Unlike the humidification process, E-SOX is independent of the presence of upper furnace sorbent injection. It involves removal of an ESP field to provide a reaction and drying chamber for an injected sorbent slurry. The addition of cold-pipe prechargers and larger wires upgrades the remaining ESP sections to maintain particulate control. Although the aqueous phase capture mechanisms are essentially the same as duct spraying, E-SOX uses unreacted $Ca(OH)_2$ in a slurry, eliminating the neccessity of sorbent scavenging. SO_2 removal of 40 to 65% is possible with a $Ca(OH)_2$ sorbent, while removal of over 90% occurs with sodium carbonate as the reagant (Sparks et al., 1985).

The reaction/drying chamber typically allows for 1 to 2 s residence time for reaction and drying of the injected slurry. Incomplete drying can severly degrade ESP performance, and so small droplet sizes are desirable for fast evaporation (Sparks et al., 1986). Modeling efforts have adapted a spray drier model by Damle and Sparks (1984) to aid performance predictions. Model predictions indicate that slurry droplets less than 30 μm allow for evaporation and significant SO_2 reduction in the available residence time.

Experimental testing shows that reaction occurs while the particle remains in the aqueous phase, as with duct spraying. Pilot-scale testing by Sparks et al. (1985) showed that the initial SO_2 removal rate is quite high, exceeding 50% SO_2 removal (at Ca/S = 2) within 500 ms. During this period, the rate of removal is apparently limited by the rate of lime dissolution into the droplet. At longer time corresponding to droplet drying, the removal rate declines quickly.

The effect of higher SO_2 concentration is to increase reactivity up to about a Ca/S ratio of 1.5 (Sparks et al., 1986). Beyond this, little additional capture is noted, suggesting that the reaction is likely limited by calcium availability.

Current research efforts are aimed at understanding the effects of Ca/S ratio, approach to saturation, slurry solids concentration, and droplet size upon reaction. Process optimization is being investigated through the use of solids dispersants to prevent in-droplet sorbent agglomeration, enhancement of calcium mass transfer, and pH buffers to encourage calcium dissolution.

SUMMARY

Three processes for SO_2 removal have been examined for their technical development, process limitations, and areas requiring further development. Upper furnace injection of dry calcium-based sorbents has been extensively investigated, although significant questions still remain on the mechanistic level. Use of $Ca(OH)_2$ sorbents under favorable conditions is expected to result in SO_2 captures around 50 to 60% at Ca/S = 2.0. The process of duct spraying was developed to enhance the upper furnace capture of SO_2. This is expected to bring a fractional increment of added capture, although reliable estimates are impossible due to the lack of pilot or full-scale data. Retrofit duct spraying will likely be limited in its efficiency due to process limitations of wall wetting. E-SOX represents an emerging technology which shows promise for SO_2 removal, yet requires considerable research prior to its full development.

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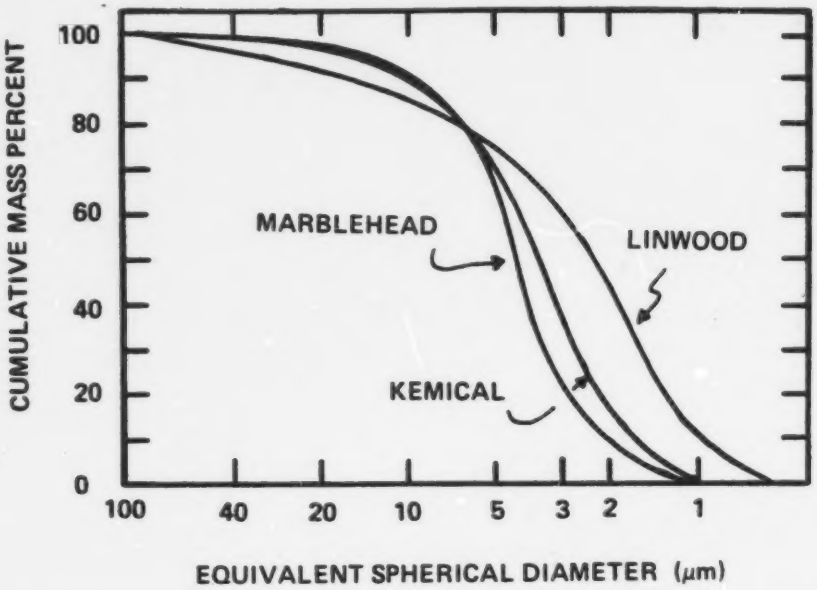

Figure 1. Particle size distributions of $Ca(OH)_2$ sorbents.

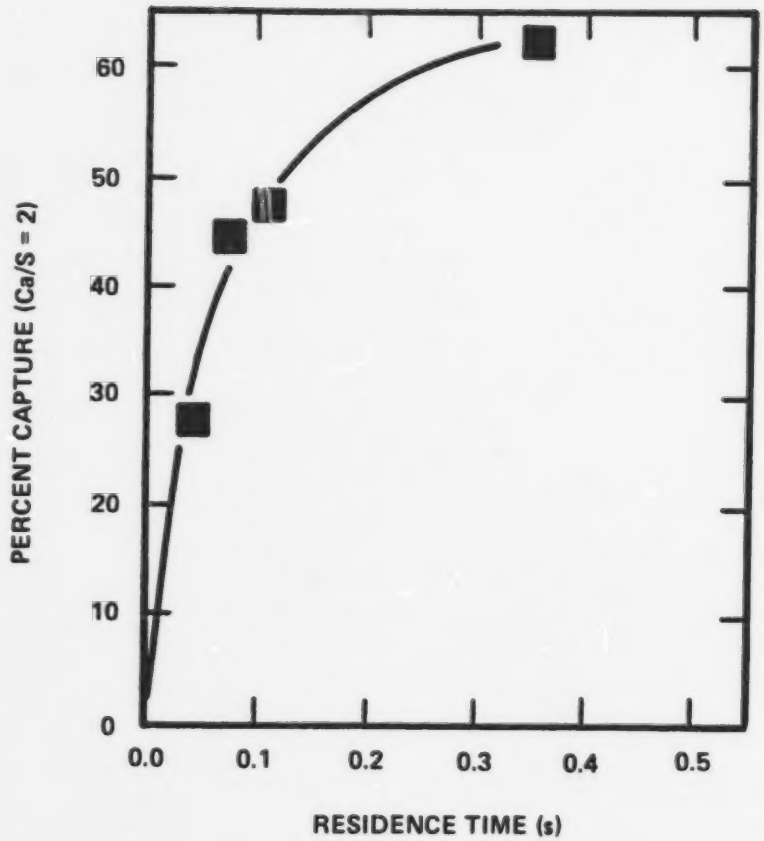

Figure 2. Short time sulfur capture at 1100°C.

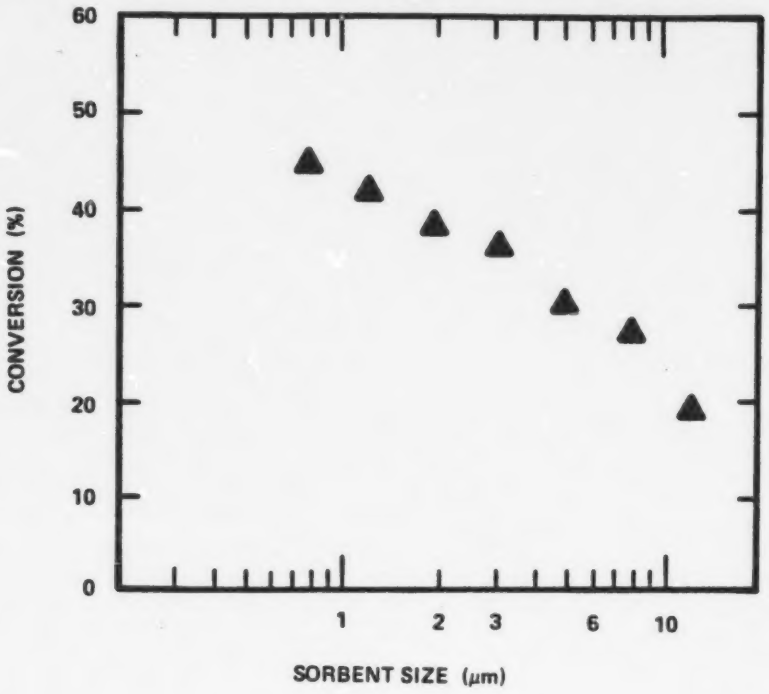

Figure 3. Effect of sorbent size upon conversion at 1100°C, 0.74 s, 3000 ppm SO_2.

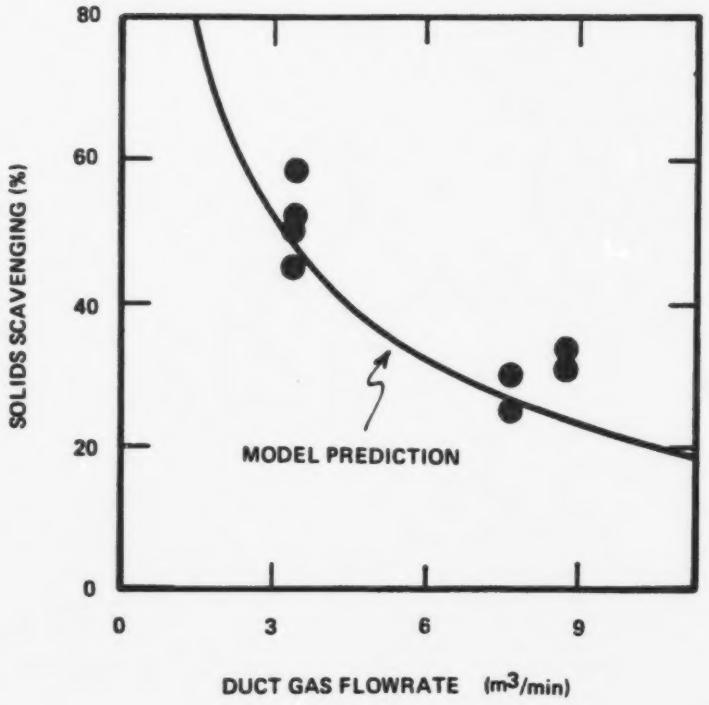

Figure 4. Experimental data and modeling results (solid line) showing the effect of duct flowrate upon scavenging.

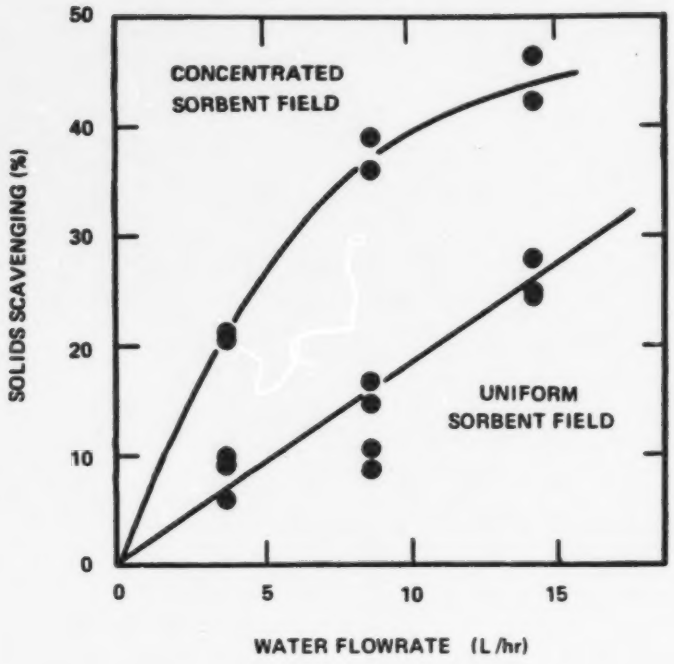

Figure 5. Effect of concentrating the sorbent field upon solids scavenging.

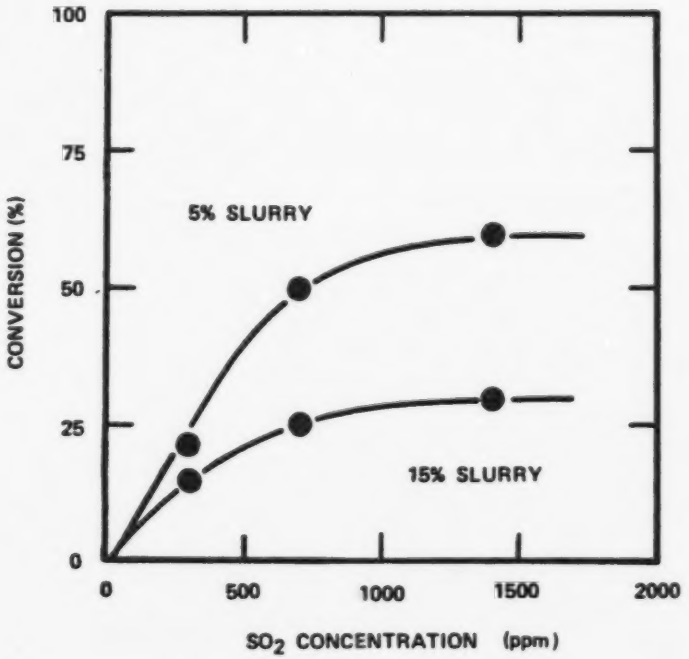

Figure 6. SO_2 concentration effect upon reaction.

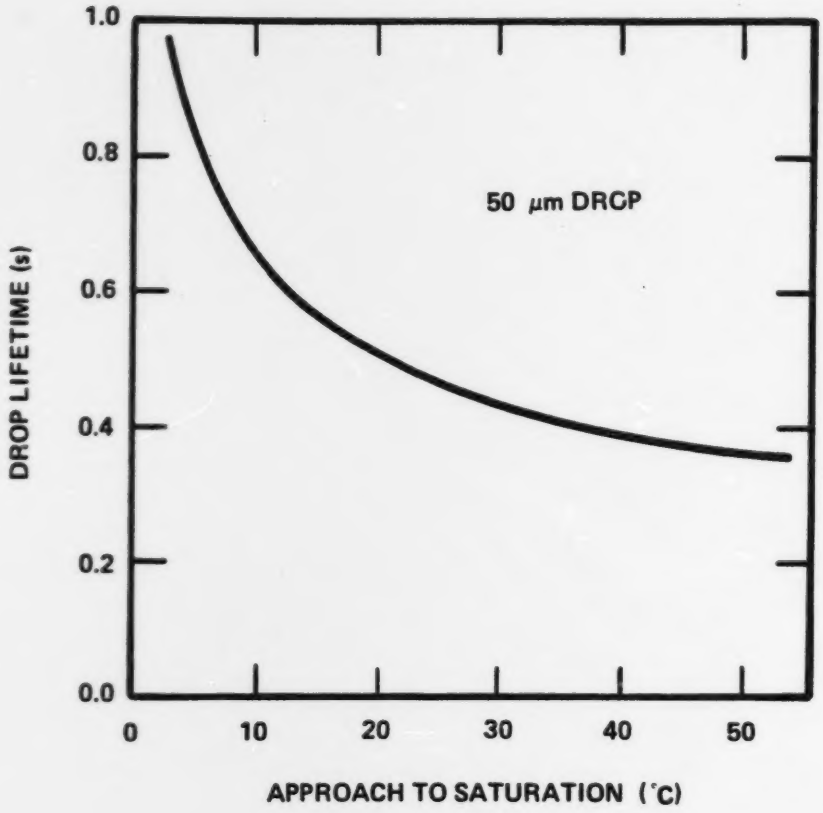

Figure 7. Model results of droplet lifetime related to the approach to saturation.